

Studies on the molecular weight dependence of tacticity of anionically prepared PMMAs by on-line GPC/NMR

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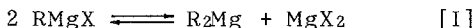
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SUMMARY

Several PMMA samples prepared in toluene with anionic initiators such as $t\text{-C}_4\text{H}_9\text{MgBr}$, $n\text{-C}_4\text{H}_9\text{MgCl}$, 1,1-diphenylhexyllithium, $t\text{-C}_4\text{H}_9\text{Li}$ and $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ complex were analyzed by the on-line GPC/NMR method using a 500 MHz ^1H NMR spectrometer as a real-time detector of GPC. The molecular weight dependence of tacticity of the PMMAs could be elucidated by this method for a short time (≤ 60 min per sample) with a small amount of the sample (≈ 1 mg). The plots of intensities of the α -methyl proton resonances due to *mm*- and *rr*-triads against elution time showed the variation of tacticity with molecular weight of the PMMA. On the basis of the results, the natures of active species in the polymerizations were discussed.

INTRODUCTION

The polymerization of methyl methacrylate (MMA) by anionic initiator such as Grignard reagents and alkyllithiums often involves multiple active species with different reactivities and stereospecificities. For instance, Grignard reagent is considered to exist in the well known Schlenk equilibrium;



and it is suggested that "RMgX" produces highly isotactic PMMA and "R₂Mg" syndiotactic PMMA (1). Aggregation of active species in the anionic polymerizations may also affect the polymerization reaction. The resulting polymer has consequently a broad and/or multimodal molecular weight distribution, and tacticity of the polymer varies with molecular weight. It is essential for the understanding of the nature of active species in these polymerizations to examine the molecular weight dependence of tacticity of the polymer. However, fractionation of polymer is usually laborious and requires considerable amount of the polymer sample.

Recent progress in NMR spectrometer on the sensitivity and resolution permitted us to combine the spectrometer with a gel permeation chromatograph. We have reported that the on-line GPC/NMR method using a 500 MHz ^1H NMR spectrometer was useful for the determination of molecular weight of polymer without calibration curve (2,3) and the structural analysis of block and random copolymers (4) and of oligomers (5). In this paper we will report the feasibility of the on-line GPC/NMR technique to the studies on the molecular weight dependence of tacticities of the PMMAs prepared by several anionic initiators.

EXPERIMENTAL

MMA was purified by fractional distillation, dried over calcium dihydride, and then distilled under high vacuum just before use. $t\text{-C}_4\text{H}_9\text{MgBr}$ and $n\text{-C}_4\text{H}_9\text{MgCl}$ were prepared from the corresponding halides and magnesium in diethyl ether. 1,1-Diphenylhexyllithium was obtained by reacting $n\text{-C}_4\text{H}_9\text{Li}$ with 1,1-diphenylethylene in toluene. $t\text{-C}_4\text{H}_9\text{Li}$ was obtained commercially as a pentane solution and used as a heptane solution. Commercial tributylaluminum was used as a heptane solution. Toluene, purified by a usual manner and stored over sodium metal, was mixed with a small amount of $n\text{-C}_4\text{H}_9\text{Li}$ and then vacuum-distilled. Polymerization was carried out in a glass ampoule under dry nitrogen atmosphere.

The on-line GPC/NMR system consisted of a JEOL JNM-GX500 spectrometer and a JASCO TRI ROTAR-V chromatograph equipped with a Shodex GPC column K-80M (30 cm x 0.8 cm, maximum porosity of 3×10^7). Further details of the system setup was described in the previous report (2). A 5 mm quartz tubing with inner diameter of 2 mm was used for the observation flow-cell (2). Chloroform- d was used as an eluent and the flow rate was 0.2 ml/min. The amount of sample injected was 1 mg each. The conditions of ^1H NMR data-acquisition were as follows: pulse angle, 60° ; pulse repetition time, 1.0 s; frequency range, 4500 Hz; data point, 8192; number of scans for single data block, 24; line broadening factor, 0.55 Hz.

RESULTS AND DISCUSSION

As we reported previously, polymerization of MMA in toluene with the $t\text{-C}_4\text{H}_9\text{MgBr}$ prepared in diethyl ether yields highly isotactic PMMA with a narrow molecular weight distribution (MWD) (6). The $t\text{-C}_4\text{H}_9\text{MgBr}$ solution contained an excess amount of MgBr_2 which was formed through the side reaction between $t\text{-C}_4\text{H}_9\text{MgBr}$ and $t\text{-C}_4\text{H}_9\text{Br}$ during the preparation. Owing to the excess amount of MgBr_2 , the Schlenk equilibrium (equation I) shifts to the side of " $t\text{-C}_4\text{H}_9\text{MgBr}$ " which produces highly isotactic PMMA. Accordingly, the isotacticity of the PMMA prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ depends strongly on the amount of MgBr_2 in the initiator solution; the $t\text{-C}_4\text{H}_9\text{MgBr}$ solution whose $\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg}$ ratio was larger than 1.5 gave highly isotactic polymer and that with the ratio less than unity gave less isotactic or syndiotactic polymer (6).

Figure 1a shows the ^1H NMR-detected GPC trace of the PMMA prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ ($\text{Mg}^{2+}/t\text{-C}_4\text{H}_9\text{Mg} = 0.87$) in toluene at -78°C . The chromatogram was obtained by monitoring the methoxy proton resonance at 3.59 ppm. The polymer has a trimodal MWD, and the ^1H NMR spectra acquired in the elution periods F₁, F₂ and F₃ (cf. Fig. 1a) show that the tacticity of the higher molecular weight part is syndiotactic (Fig. 1c) while those of the lower molecular weight parts are less syndiotactic (Fig. 1d) or stereoblock-like (Fig. 1e). The molecular weight dependence of tacticity can also be illustrated in a continuous form by plotting the signal intensities of the α -methyl proton resonances at 0.86 and 1.20 ppm due to the rr - and mm -triads, respectively, against elution time (Fig. 1b). It is very clear that the fraction of syndiotactic triad increases with an increase in molecular weight of the polymer. The results suggest that the high molecular weight part with high syndiotacticity (cf. Fig. 1c) was produced from the species generated by " $(t\text{-C}_4\text{H}_9)_2\text{Mg}$ " and that the isotactic part which has lower molecular weight and a relatively narrow MWD (cf. Fig. 1e) was produced from the species generated mainly by " $t\text{-C}_4\text{H}_9\text{MgBr}$ ".

Figure 2 shows the results of GPC/NMR analysis for the PMMA obtained

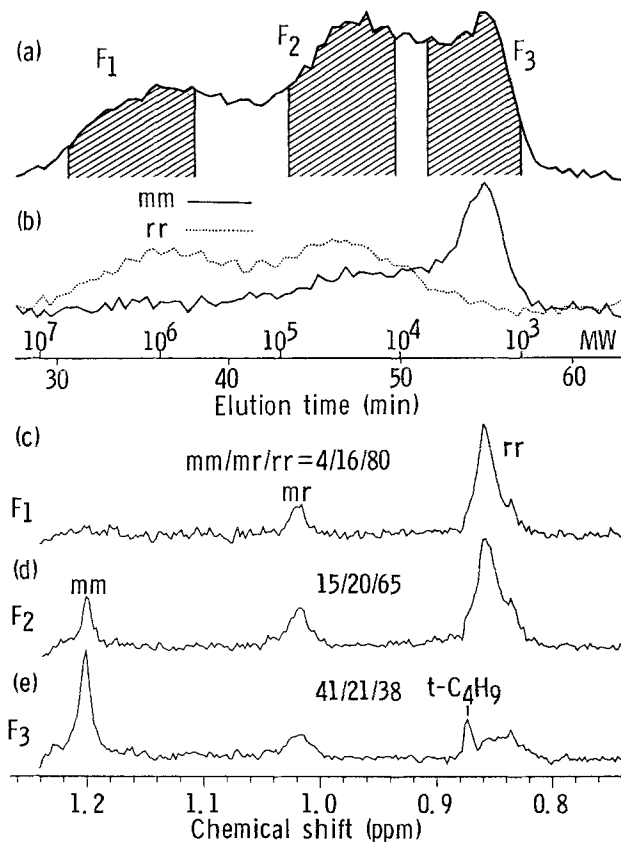


Figure 1. The ^1H NMR-detected GPC traces obtained by monitoring the methoxy proton resonance at 3.59 ppm (a) and the α -methyl proton resonances at 0.86 ppm (.....) and 1.20 ppm (—) due to *rr*- and *mm*-triads, respectively (b). The NMR signals due to α -methyl protons of the PMMA eluted in the elution periods F1 (c), F2 (d) and F3 (e) are also shown.

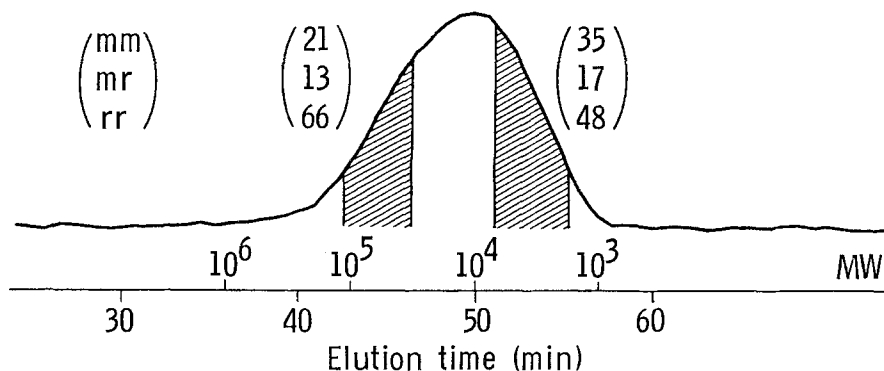


Figure 2. ^1H NMR-detected GPC trace of the PMMA prepared with $n\text{-C}_4\text{H}_9\text{MgCl}$ in toluene at -78°C (monitoring the methoxy proton resonance at 3.59 ppm) and the triad tacticities of the eluting fractions.

by $n\text{-C}_4\text{H}_9\text{MgCl}$ in toluene at -78°C (7). The Grignard reagent was also prepared in diethyl ether but contained a stoichiometric amount of Mg^{2+} ($\text{Mg}^{2+}/n\text{-C}_4\text{H}_9\text{Mg} = 1.0$). As shown in Fig. 2, the PMMA has a broad MWD and the higher molecular weight part is more syndiotactic than the lower molecular weight one. Probably the situation is similar to that of the polymerization by $t\text{-C}_4\text{H}_9\text{MgBr}$ mentioned above, although the MWD is unimodal. It was reported that PMMA formed with $n\text{-C}_4\text{H}_9\text{MgCl}$ was a mixture of isotactic and syndiotactic PMMAs as evidenced by thin layer chromatography (8) and competitive adsorption to silica gel (9). The GPC/NMR analysis clearly shows that the syndiotactic part had higher molecular weight than the isotactic one.

The PMMA prepared with 1,1-diphenylhexyllithium (DPHLi) in toluene at -78°C is highly isotactic. However, the MWD of the polymer is very broad. GPC/NMR analysis revealed that the isotacticity of the polymer increased with increasing molecular weight and that the high molecular weight part was almost 100 % isotactic in triad (Fig. 3). The results indicate that the reactivity of the propagating species has a wide distribution and the species with the higher reactivity are more isotactic-specific. The difference in the structure of the propagating species may be caused partly by the association among the DPHLi molecules in toluene at low temperature. The number average molecular weight of the polymer was much larger than the theoretical value calculated from the polymer yield and the initial monomer/initiator ratio, which indicates the association of DPHLi. Wiles and Bywater (10) reported a similar variation of isotacticity with molecular weight for the PMMA formed with DPHLi in toluene at -30°C ; the isotactic triad contents in fractionated PMMAs varied from 75 % ($M_v = 10^4$) to 95 % ($M_v = 10^6$).

Polymerization of MMA with $t\text{-C}_4\text{H}_9\text{Li}$ in toluene at -78°C gave isotactic-rich PMMA with a broad but unimodal MWD (11,12). Figure 4 shows an NMR-detected GPC trace and a variation of isotactic triad content with molecular weight. Similarly to the DPHLi-initiated polymerization, the isotacticity increased with increasing molecular weight. However, the distribution of the propagating species in regard to reactivity in the polymerization by $t\text{-C}_4\text{H}_9\text{Li}$ seems much narrower than that in the polymerization by DPHLi. The difference may result from different degree of association of these initiators.

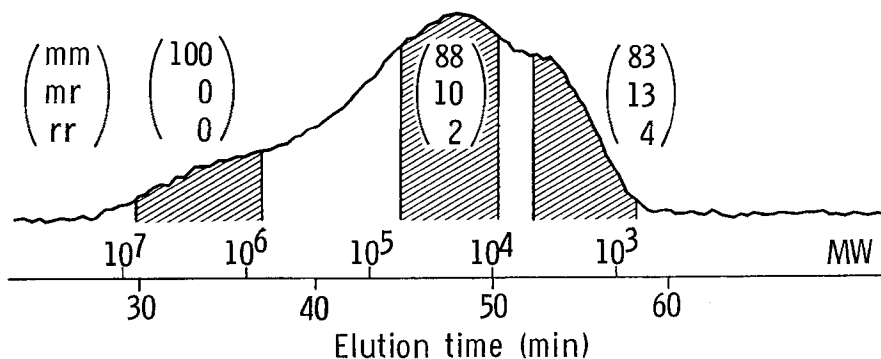


Figure 3. ^1H NMR-detected GPC trace of the PMMA prepared with 1,1-diphenylhexyllithium in toluene at -78°C (monitoring the methoxy proton resonance at 3.59 ppm) and the triad tacticities of the eluting fractions.

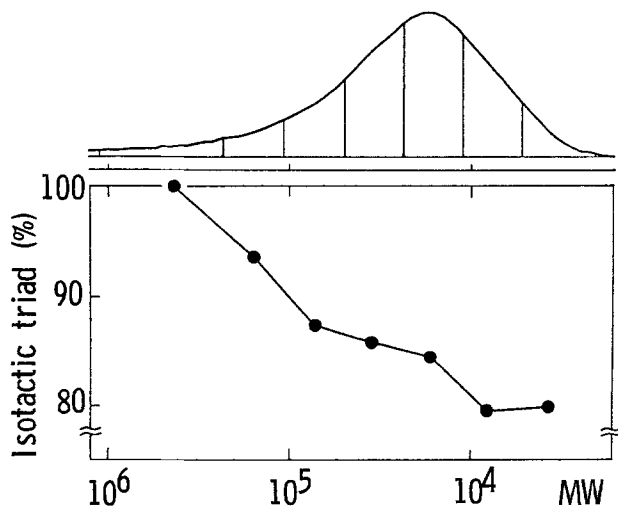


Figure 4. ^1H NMR-detected GPC trace of the PMMA prepared with $t\text{-C}_4\text{H}_9\text{Li}$ in toluene at -78°C and the plot of the mm -triad content for the seven regions.

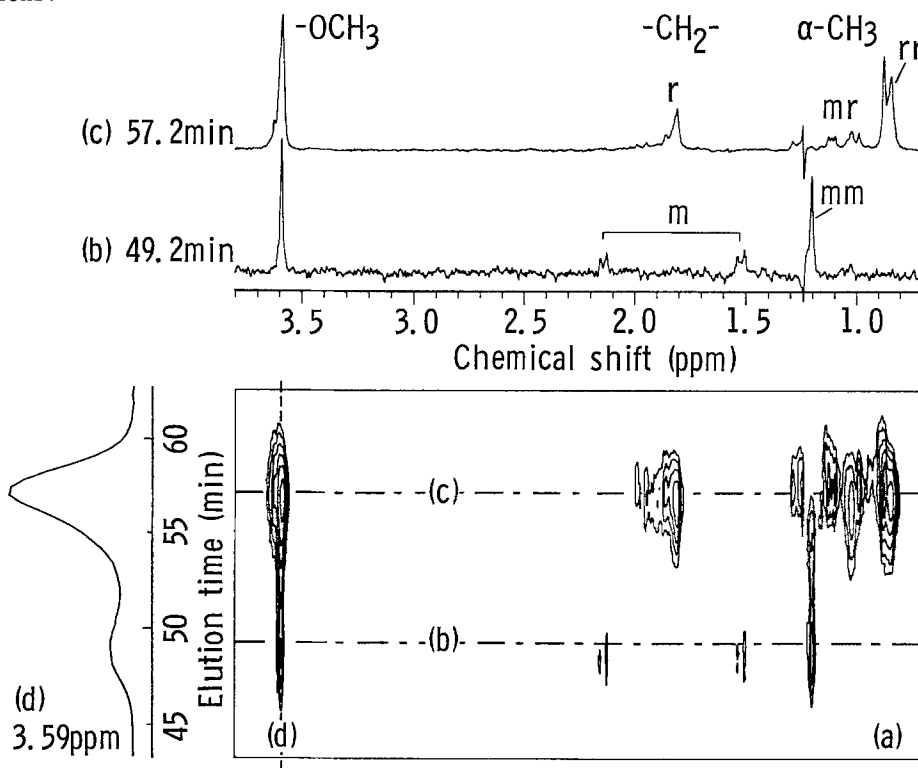


Figure 5. A contour plot (a) and cross sections (b-d) of the on-line GPC/NMR data for the PMMA prepared with $t\text{-C}_4\text{H}_9\text{Li}$ - $(n\text{-C}_4\text{H}_9)_3\text{Al}$ ($\text{Al}/\text{Li} = 1.0$) in toluene at -78°C .

It was recently found that a mixture of $t\text{-C}_4\text{H}_9\text{Li}$ and trialkylaluminum (R_3Al) such as triethyl-, tri- n -butyl- or tri- n -octylaluminum gave highly syndiotactic polymers of MMA and other methacrylates with narrow MWD in toluene at low temperatures (11,12). As described above, $t\text{-C}_4\text{H}_9\text{Li}$ itself gave an isotactic PMMA with a broad MWD. Addition of R_3Al increased the syndiotacticity of the PMMA and at the ratio of $\text{R}_3\text{Al}/t\text{-C}_4\text{H}_9\text{Li} \geq 3$ highly syndiotactic PMMAs with a narrow MWD were produced. At the ratio of 1.0 the PMMA with stereoblock-like tacticity and with a bimodal MWD formed in a low yield.

The PMMA prepared with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ ($\text{Al}/\text{Li} = 1.0$) in toluene at -78°C was analyzed by on-line GPC/NMR as shown in Fig. 5. Figure 5a is a contour plot of the GPC/NMR data and the spectra of the cross section at 49.2 and 57.2 min are shown in Figs. 5b and 5c (12), respectively. These clearly indicate that the lower molecular weight part is syndiotactic and the higher molecular weight one is highly isotactic. Addition of R_3Al to $t\text{-C}_4\text{H}_9\text{Li}$ generates syndiotactic propagating species for MMA by the formation of a weak complex between $t\text{-C}_4\text{H}_9\text{Li}$ and $(n\text{-C}_4\text{H}_9)_3\text{Al}$ and at the ratios of $\text{Al}/\text{Li} \geq 3$ all the $t\text{-C}_4\text{H}_9\text{Li}$ molecules are involved in the syndiotactic species. At the ratio of 1.0 there exist isotactic and syndiotactic propagating species concomitantly to give a mixture of isotactic and syndiotactic PMMAs. The mixture forms stereocomplex in toluene at low temperature so that the polymerization mixtures gels, which causes the low yield of the polymer.

The results mentioned in this paper demonstrate the usefulness of the on-line GPC/NMR for the analysis of molecular weight dependence of tacticity. The method contributes greatly to the understanding of the mechanism of stereoregulation in polymerization, and an extensive study is now under way.

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